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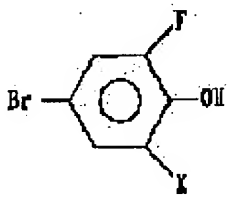
(54) HIGHLY FLUORINATED PHENYLPROPYL ETHER AND ITS PRODUCTION

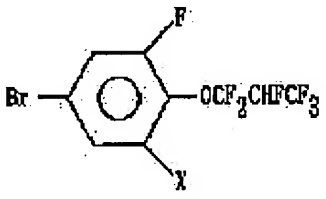
(57)Abstract:

PURPOSE: To readily produce the subject new highly fluorinated compound useful as a raw material for chemically synthesizing liquid crystals, medicines agrochemicals, etc., by reacting a phenolic compound with hexafluoropropene.



I

CONSTITUTION: A phenolic compound of formula I (X is H, F, Cl) (e.g. 4- bromo-2-fluorophenol) is charged in a reaction container equipped with a gas- blowing port, a gas exhaust port and a thermometer, mixed with a polar solvent such as N,N-dimethylformamide and an alkali catalyst such as potassium hydroxide, and subsequently reacted with hexafluoropropene charged from the gas-blowing port under stirring for 1-6hrs. The reaction solution is mixed with water to separate the organic phase, which is separated, concentrated under vacuum and purified by a distillation method, etc., to provide the objective highly fluorinated phenylpropyl ether expressed by formula II, useful as a raw material for chemical synthesizing liquid crystals, medicines, agrochemicals,



II

etc.

LEGAL STATUS

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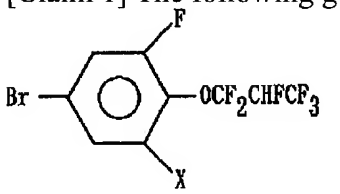
* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

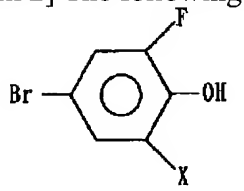
CLAIMS

[Claim(s)]
[Claim 1] The following general formula [** 1]



(XはH, FまたはCl)

The altitude fluorination phenylpropyl ether come out of and expressed.
[Claim 2] The following general formula [** 2]



(XはH, FまたはCl)

The manufacturing method of the altitude fluorination phenylpropyl ether according to claim 1 characterized by coming out and making the phenolic compound expressed react with a hexafluoro propene.

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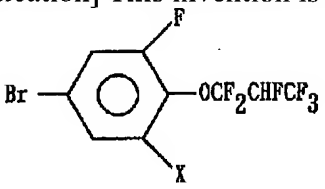
* NOTICES *

DETAILED DESCRIPTION

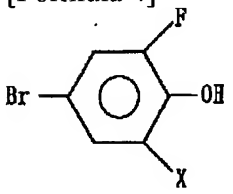
[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention is the following general formula. [Formula 3]



(XはH, Fまたは Cl)

The advanced fluorination phenylpropyl ether come out of and expressed, i.e., 4-BUROMO-2-fluoro phenyl, - 1, 1, 2, 3, 3, and 3-hexafluoro propyl ether (X=H), 4-BUROMO -2, 6-difluoro phenyl - The 1, 1, 2, 3, 3, and 3-hexafluoro propyl ether (X=F) or 4-BUROMO-2-chloro-6-fluoro phenyl - It is related with the 1, 1, 2, 3, 3, and 3-hexafluoro propyl ether (X=Cl) and its manufacturing method. These compounds are new molecular entities of reference non-**, and are useful as raw materials, such as the raw material for chemosynthesis, for example, liquid crystal, physic, and agricultural chemicals.
[0002]
[Description of the Prior Art] In recent years, many things depended on a liquid crystal display as a display of television, a personal computer, a word processor, etc. have come to be adopted. As a liquid crystal ingredient used for these liquid crystal display components, since what introduced the fluorine atom into the end of a molecule has that charge retention is high-reliability greatly and low viscosity, a response has the remarkable descriptions, such as a quick thing, and is effective in especially a active-matrix drive method. Therefore, the compound concerned can be used as synthetic powder of useful liquid crystal by carrying out a coupling reaction in a bromination base (see Mol.Cryst.Liq.Cryst., 1991, Vol.204, pp 77-89 and a functional material, 1991, Vol.11, and No2, pp5 - 12 grades).
[0003] Moreover, since raising bioactive since the unique property-electronegativity of a fluorine atom of a fluorine-containing compound is large, and an atomic radius are close to it of a hydrogen atom, it is used as physic and an object for agricultural chemicals using -, such as being easy to incorporate a living body, (for example, fluorine physiological active substance CMC ****** of the 90s).
[0004] For example, it is actually permutation phenyl. - The 1, 1, 2, 3, 3, and 3-hexafluoro propyl ether compound shows effect as a high activity insecticide (for example, refer to JP,3-4543,B and JP,3-47159,A). Therefore, the compound concerned can also be used as a raw material of a physiological active substance.
[0005]
[Problem(s) to be Solved by the Invention] The purpose of this invention is offering a new altitude fluorination phenylpropyl ether compound and its process.
[0006]

[Means for Solving the Problem] We are general formulas as a result of wholeheartedly research.
[Formula 4]



(XはH, FまたはCl)

It found out that the new altitude fluorination phenylpropyl ether which comes out and is applied to this invention by the reaction of phenol derivatives, such as the 4-BUROMO-2-fluorophenol and 4-BUROMO -2 which are expressed, a 6-difluoro phenol, or 4-BUROMO-2-chloro-6-fluorophenol, and a hexafluoro propene was compoundable.
[0007] 4-BUROMO-2-fluorophenol is obtained by performing diazotation, hydrolysis, and bromination with a conventional method from o-fluoro aniline currently industrially made as a drugs raw material, and 4-BUROMO -2 and a 6-difluoro phenol are obtained with a conventional method from a 2 and 6-difluoro aniline by the hydrolysis which continues with chlorination by the Sandmeyer's reaction. Moreover, 4-BUROMO-2-chloro-6-fluorophenol can be chlorinated with a conventional method, and can obtain the above-mentioned 4-BUROMO-2-fluorophenol. On the other hand, the hexafluoro propene is industrially made as a raw material of a perfluoro polyether useful as a lubricating oil.
[0008] An example of composition of the altitude fluorination phenylpropyl ether of this invention melts the above phenol derivatives to a solvent first, and adds an alkali catalyst. Blow a bottom of ordinary pressure hexafluoro propene there, it is made to react to it, and the compound concerned is obtained. Various organic solvents can be used as a solvent of this reaction. Inorganic alkali and organic amines can be used as a catalyst. In the case of inorganic alkali, mol addition is carried out 0.05 to 0.2 times to the phenol concerned. On the other hand, in the case of organic amines, mol addition is carried out 0.2 to 1.5 times.
[0009] Especially, using polar solvents, such as N.N-dimethylformamide and N-methyl pyrrolidone, when inorganic alkali catalysts which dissolved in water, such as a sodium hydroxide and a potassium hydroxide, are used, the specified substance is obtained with yield with them. [there are few by-products and good]
[0010] Moreover, when using chlorine-based solvents, such as ether, such as ethyl ether and isopropyl ether, and dichloromethane, chloroform, and other solvents insoluble in water, organic amines, such as triethylamine and a pyridine, are used as a catalyst. In this case, compared with the former, they are 4-BUROMO-2-fluoro phenyl and 4-BUROMO. - 2 and 6-difluoro phenyl or 4-BUROMO-2-chloro-6-fluoro phenyl - 1, 1, 2, 3, 3, and 3-pentafluoro-1-propenyl ether, And 4-BUROMO-2-fluoro phenyl, 4-BUROMO -2, 6-difluoro phenyl, or 4-BUROMO-2-chloro-6-fluoro phenyl - It becomes the inclination whose by-products, such as the 1, 1, 2, 3, 3, and 3-pentafluoro-2-propenyl ether, increase. A compound and the boiling point concerned are approaching and removal by distillation is not easy for these by-products. Therefore, the combination of a polar solvent and an inorganic alkali catalyst is more desirable.
[0011] The reaction temperature of the reaction concerned has 10 degrees C - preferably good 80 degrees C below the boiling point of 5-degree-C or more solvent. If a reaction rate becomes slow and it is too high when reaction temperature is low, a by-product will increase. Since a reaction is a vapor-liquid reaction, it is desirable to improve contact of vapor-liquid, such as churning. A reaction progresses at sufficient rate by performing the flow rate when blowing a hexafluoro propene with extent in which exhaust gas does not appear from a reactor.
[0012] After a reaction, although water is added and dissolution removal of the alkali catalyst is carried out, when water-soluble solvents, such as N.N-dimethylformamide, are used, a product is extracted using an insoluble solvent in water, such as after [addition] isopropyl ether of water, and

dichloromethane. An organic phase is washed with water until wash water becomes neutrality. Next, the compound concerned is obtained by carrying out evaporation removal of the solvent after dehydration by a salt cake etc.
[0013] Distillation purification is carried out for obtaining a high grade article.
[0014] Hereafter, an example explains concretely. However, this invention is not limited to this.
[0015]
[Examples 1-12] It is specified quantity ON **** about the phenol derivative (the 4-BUROMO-2-fluorophenol, 4-BUROMO -2, the 6-difluoro phenol, or 4-BUROMO-2-chloro-6-fluorophenol), solvent, and alkali catalyst (water is added when a catalyst does not melt into a solvent) of a raw material to 100ml ********** equipped with gas entrainment opening, gas exhaust, and thermometer insertion opening which were prolonged in liquid.
[0016] It is immersed in a water bath and a flask is agitated by the rotator using a magnetic stirrer.
[0017] From gas entrainment opening, a hexafluoro propene is introduced and a reaction is started. Let the flow rate of a hexafluoro propene be extent exhaust gas is not accepted to be. A reaction is finished with a 1.02-1.1Eq hexafluoro propene. Reaction time is 1 - 6 hours.
[0018] The water of reaction mixture and tales-doses extent is added after reaction termination. When a solvent is water solubility, isopropyl ether is added a tales-doses grade with water. It moves to a separating funnel and separation removal of the after [shaking] aqueous phase is carried out. Water is added to an organic phase in a separating funnel, and it washes repeatedly until wash water becomes neutrality. Vacuum concentration is carried out after dehydration and by the evaporator by the salt cake, and a rough product is obtained.
[0019] Next, it is 4-BUROMO-2-fluoro phenyl by distillation. - The 1, 1, 2, 3, 3, and 3-hexafluoro propyl ether, 4-BUROMO -2, 6-difluoro phenyl - The 1, 1, 2, 3, 3, and 3-hexafluoro propyl ether or 4-BUROMO-2-chloro-6-fluoro phenyl - The refined material of the 1, 1, 2, 3, 3, and 3-hexafluoro propyl ether is obtained. The physical-properties value of this matter is as follows.
[0020] 4-BUROMO-2-fluoro phenyl - 1, 1, 2, 3, 3, and 3-hexafluoro propyl ether 1 H-NMR (a solvent CDCl3, internal standard Me4Si)
delta5.05ppm (1H, m), 7.1-7.45 ppm (3H, m)
19 F-NMR (a solvent CDCl3, external standard CFCl3)
delta-75 ppm (3F) - 79 ppm (2F) - 125 ppm (1F) - 212 ppm (1F)
Boiling point; 100-101 degrees C (30mmHg)
Elemental analysis (%) C9H4BrF7O C H Br F Theoretical value 31.70 1.18 23.43 39.00 Analysis value 31.62 1.19 23.31 39.234-BUROMO -2, 6-difluoro phenyl - 1, 1, 2, 3, 3, and 3-hexafluoro propyl ether 1 H-NMR (a solvent CDCl3, internal standard Me4Si)
delta5.05ppm (1H, m), 7.25 ppm (2H, m)
19 F-NMR (a solvent CDCl3, external standard CFCl3)
delta-75 ppm (3F) - 79 ppm (2F) - 122 ppm (2F) - 212 ppm (1F)
Boiling point; 103-104 degrees C (30mmHg)
Elemental analysis (%) C9H3BrF8O C H Br F Theoretical value 30.11 0.84 22.26 42.33 Analysis value 30.15 0.82 22.35 42.204-BUROMO-2-chloro-6-fluoro phenyl - 1, 1, 2, 3, 3, and 3-hexafluoro propyl ether 1 H-NMR (a solvent CDCl3, internal standard Me4Si)
delta5.05ppm (1H, m), 7.3-7.5 ppm (2H, m)
19 F-NMR (a solvent CDCl3, external standard CFCl3)
delta-75 ppm (3F) - 79 ppm (2F) - 120 ppm (1F) - 212 ppm (1F)
Boiling point; 96-97 degrees C (9mmHg)
Elemental analysis (%) C9H3BrClF7O C H Br Cl F Theoretical value 28.79 0.81 21.28 9.44 35.42 Analysis value 28.55 0.82 21.55 9.50 35.11 experimental results are shown in Table 1.
[0021]
[Table 1]

No.	原料	溶媒	触媒	反応温度	反応時間	収量	収率
1	BFP 38.2g	DMF 70ml	NaOH 0.8g	20℃	2.0hr	63.0g	92.5%
2	BFP 38.2g	DMF 70ml	KOH 1.1g	20℃	2.5hr	62.4g	91.6%
3	BFP 38.2g	DMF 70ml	トリエチルアミン 15.0g	20℃	3.5hr	60.3g	88.5%
4	BFP 38.2g	DMF 70ml	NaOH 0.8g	60℃	3.0hr	58.5g	85.9%
5	BFP 38.2g	DMF 70ml	NaOH 0.8g	20℃	2.5hr	62.1g	91.2%
6	BFP 38.2g	IPE 70ml	トリエチルアミン 15.0g	20℃	3.0hr	59.8g	87.8%
7	BFP 38.2g	DCM 70ml	トリエチルアミン 15.0g	20℃	3.5hr	58.9g	86.5%
8	BDFP 41.8g	DMF 70ml	NaOH 0.8g	20℃	1.5hr	65.6g	91.4%
9	BDFP 41.8g	DMF 70ml	トリエチルアミン 15.0g	20℃	3.0hr	63.4g	88.3%
10	BDFP 41.8g	IPE 70ml	トリエチルアミン 15.0g	20℃	2.5hr	60.8g	84.7%
11	BCFP 45.1g	DMF 70ml	NaOH 0.8g	20℃	1.5hr	68.2g	90.8%
12	BCFP 45.1g	DMF 70ml	トリエチルアミン 15.0g	20℃	3.0hr	66.5g	88.5%

Notes BFP; 4-BUROMO-2-fluorophenol BDFP;4-BUROMO -2, 6-difluoro phenol DMF; N.N-dimethylformamide NMP; N-methyl-2-pyrrolidone IPE; isopropyl ether DCM; dichloromethane No.1, and 2, 4, 5, 8 and 11 add 4ml of water. [0022]

[Effect of the Invention] With the altitude fluorination phenylpropyl ether compound of this invention, composition of the useful matter can attain easily.

[Translation done.]